

NBSIR 74-510

Effect of Phase Separation on the Physical and Chemical Properties of Glasses-Density and Chemical Durability

Joseph H. Simmons, Susan A. Mills and Barbara F. Howell

Inorganic Materials Division
Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

July 1974

Final Technical Report

Prepared for
Office of Naval Research
Contract Naonr 12-73, NR 032-536
Department of the Navy
Code 471
Washington, D. C. 20360

NBSIR 74-510

**EFFECT OF PHASE SEPARATION ON THE
PHYSICAL AND CHEMICAL PROPERTIES OF
GLASSES-DENSITY AND CHEMICAL DURABILITY**

Joseph H. Simmons, Susan A. Mills and Barbara F. Howell

Inorganic Materials Division
Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

July 1974

Final Technical Report

Prepared for
Office of Naval Research
Contract Naonr 12-73, NR 032-536
Department of the Navy
Code 471
Washington, D. C. 20360



U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

1. Introduction

A number of technical glasses either undergo liquid-liquid phase separation in their annealing range or have compositions bordering on miscibility gaps. Some of these find extensive applications in the chemical ware and window glass industry, and while their usefulness for normal duty seems not to be greatly affected by the phase transitions, it is likely that special applications such as long anneals or long exposure to corrosive environments will dictate heat treatments with a combination of times and temperatures favorable for the development of large internal structure. In order to better understand the processes involved and to characterize the related changes in physical and chemical properties, an investigation of the results of heat treatments which maximize the phase separation effects in these glasses was undertaken.

In a previous series of reports¹⁻⁴ we considered the mechanism of phase separation and its effects on viscous flow processes in two borosilicate glasses of which one is commonly used for chemical ware. The results are described and analyzed in detail in our Annual Technical Report of September 1973,¹ and in a paper in the Journal of the American Ceramic Society.² We found that extensive phase separation occurs in both glasses near the annealing region and the viscosity undergoes increases 10,000 to 100,000 fold during an isothermal heat treatment. In the analysis of these results, a theory was developed which accounts for the viscosity change in terms of microstructure development in the molten glass.

The large increase in viscosity upon phase separation will affect annealing schedules by changing the rate of stress-release. For example, one of the glasses investigated, Type I in Refs. 1 and 2, has a complex time and temperature dependence for viscosity in the annealing range. This is demonstrated in figure 1 where the isothermal viscosity at 600°C is higher than at 560°C for times between 10 and 100 minutes. This unusual behavior indicates that isothermal heat treatments at 560°C will release internal stresses at a faster rate than at the higher temperature for treatments shorter than 100 minutes. At 560°C, the microstructure development is slower than at 600°C providing an additional benefit for the lower temperature anneal. If a long heat treatment is needed, then an increase in temperature to 600° or 620°C after 100 min. will be desirable.

Having characterized the microstructure development and the stress relaxation mechanism, we have proceeded to measure the effect of pressure on phase separation, and to measure the loss of chemical durability accompanying the two-phase formation. The potential effect of pressure or stress on the thermodynamic conditions controlling phase separation are reflected in the behavior of the density, refractive index and thermal expansion coefficient. The chemical durability of an alkali containing glass can be measured by the amount of alkali released from the glass when exposed to the desired chemical environment. Of the

two glasses studied in the early part of this work^{1,2} only Type II, the glass commonly used for chemical ware, is suitable for this study. Type I, the simple sodium-borosilicate glass suffers too large a loss in chemical durability during phase separation to provide for a convenient analysis by the means contemplated here. Further, its poor durability will greatly complicate the density measurements since the density liquids are likely to alter its chemical makeup. Therefore, below, we report measurements of density, index of refraction, thermal expansion coefficient and chemical durability on the Type II glass only. The stress relaxation time for this glass during phase separation is shown in figure 2.

2. Experimental Section

2.1 Glass Samples

The glass chosen (Type II in our previous work^{1,2}) has a composition consisting of SiO_2 , B_2O_3 , Na_2O and Al_2O_3 in the proportions: 81:12.6:3.9:2.4 by weight, as determined by chemical analysis. Its phase transition temperature is 649°C where its viscosity is 10^{11} poises. It separates into a phase which is almost exclusively silica and alumina with a volume fraction of 0.55. The second phase, rich in soda and boron trioxide occupies a volume fraction of 0.45.

The samples were in the form of rectangles 0.1x0.6x1.0 cm for the density and index of refraction tests and rods 1/4" by 2 cm long for the thermal expansion coefficient tests.

2.2 Index Measurements

The samples were heat treated in a furnace with an inconel core. The samples were dropped into and out of the furnace, thus effecting a rapid temperature change in each case. The reproducibility of the quench was checked by heat treating several samples at the same temperature and comparing the index differences. No discrepancy was found between the readings.⁵

A Grauer Refractometer was used to measure the index of refraction. The data for isothermal heat treatments between 526° and 620°C are shown in figure 3.

2.3 Density Measurements

The samples were heat-treated in the same manner as for the index measurement. The density was measured using the sink-float technique by immersing the samples in a thermostatically controlled density liquid. The latter was a mixture of Iso-Propyl Salicylate (38.1%) and s-Tetrabromoethane (61.9%).⁶ The liquid mixture was calibrated with two density standards giving the values 2.22000 at 27.396°C and 2.23250 at 21.495°C. This yielded the following equation:

$$\rho = 2.22000 - 0.002118(T - 27.396) \quad (1)$$

where ρ is in g/cm^3 and T in °C. The temperature was measured with a 4-lead Pt resistance thermometer calibrated at NBS with a constant current of 1.0 ma through the thermometer.

The measurement was effected by slowly raising the temperature of the bath (.0035°C/min) and recording the temperature at which the sample changed from a floating to a sinking condition. The sample was restrained 6 cm below the surface of the density liquid in order to avoid evaporative

cooling effects.

The accuracy of the measurement depends directly upon the density standards which were certified to $\pm .0005 \text{ gr/cm}^3$ by the manufacturer* but not verified by us. The precision of the measurement is approximately $\pm 3 \times 10^{-6} \text{ g/cm}^3$ or $\Delta\rho/\rho = \pm 1.5 \times 10^{-6}$.

Samples were measured and heat treated in succession. Several samples were used for each isothermal study but none were heat treated at more than one temperature. The resulting isothermal density data is plotted as a function of heat-treatment time in figures 4 and 5.

2.4 Thermal Expansion Coefficient Measurement.

The coefficient of thermal expansion was measured in a modified beam-bending viscometer.⁷ The cylindrical samples were placed in an inconel box within a furnace, and the expansion of the glass during heating was measured by recording the position of a long silica rod resting on top of the sample cylinder with the sensing element of a linear deflection transducer attached to the other end. A concentric silica cylinder resting on the box was used to support the outer portion of the transducer. This arrangement allowed a measurement of the difference between the expansion of the sample and an equal length of silica.

The furnace was heated at 2°C per minute and the temperature was monitored with a Pt-10% Pt-Rh thermocouple touching the sample. Temperature gradients within the chamber were less than 5°C . The transducer output was recorded on the y-axis and the voltage generated by the thermocouple on the x-axis of a recorder. A typical expansion curve thus obtained is shown in figure 6.

The glass samples were first heat treated between 565° and 620°C for a variety of times, and then were tested for a measurement of the coefficient of thermal expansion. The data is shown in figure 7.

2.5 Chemical Durability Measurement

The measure of resistance of glass to chemical attack is highly subjective to the test performed. Therefore, we decided to use the ASTM durability test.⁸ While the chemical processes involved in this

* R. P. Cargille Laboratories, Inc., Cedar Grove, N.J. 07009.

test are complicated, we chose it because of its wide use in industrial plants and, therefore, the ease in relating the data to that obtained in industry and the possibility of a comparison with other materials.

The experimental procedure is described in detail in Refs. 8 and 9. Briefly, the glass samples in the form of 1/4-inch rods were heat-treated at 565°, 585°, 600°, 620° and 640°C for selected time periods, and crushed to form powders of a desired size (40 to 50 mesh sieves). The powder was covered with water and autoclaved at 121°C for 30 minutes. Subsequently, the amount of alkali released in the water during autoclaving was determined with a dilute standardized sulfuric acid solution using methyl red as indicator.

This technique gives a good account of the amount of material leached out during the autoclave treatment since the boric and silicic acids formed are expected to be small in content and weak compared to the sodium hydroxide base. However, in order to measure the Si, B and Al released, we are preparing to test the released solutions with an Atomic Absorption Spectrometer. The instrument has been ordered and the measurements will be conducted next fiscal year. The results of the titration test are shown in figure 8 and demonstrate a large (100 fold) decrease in the resistance of this material to chemical attack when phase separation occurs.

3. Analysis Section

3.1 Pressure Effect

3.1.1 Theory

The volume change resulting from phase separation can be analyzed to yield the change in phase transition temperature due to applied pressure or stress on the glass. The transition temperature can be expressed in terms of the mixing enthalpy and entropy and the concentrations of the phases by means of Regular Mixing Equations.¹⁰ We have shown that, with proper choice of phase compositions, the miscibility gaps of binary¹¹ and ternary¹² systems can be described by means of the regular mixing concepts. If the glass only separates into two phases, as we have observed for this particular material over the temperature range 540° to 660°C,¹ then the transition temperature θ can be expressed as:

$$\theta = \frac{\Delta H}{R} f(y_i) \quad (2)$$

where $f(y_i)$ is a complex function of the molar concentrations of the component oxides and ΔH is the enthalpy of mixing for the system. At the critical composition of the system, the transition temperature θ_c , often called the critical temperature, is expressed as:

$$\theta_c = \frac{\Delta H}{2R} \quad (3)$$

The critical composition is defined as the composition where the separate phases are at equal fractional concentrations. In most cases this corresponds to the glass which separates into phases of equal volume fractions. The critical temperature is the highest transition temperature achieved by the mixture of the same phases in any possible proportion.

The effect of pressure applied at constant temperature on the phase transition is found by differentiating θ as follows:

$$\left(\frac{\partial \theta}{\partial P}\right)_T = \left(\frac{\partial \Delta H}{\partial P}\right)_T f(y_i) / R \quad (4)$$

Using a Legendre Transformation and defining the volume coefficient of thermal expansion as $\alpha = (\partial v / \partial T)_P / v$, the change in phase transition temperature may be expressed as:

$$\left(\frac{\partial \theta}{\partial P}\right)_T = \frac{\Delta H(T)}{2R \theta_c / \theta} [1 - T \alpha] \quad (5)$$

where $\Delta v = v_{\text{mix}} - v_{\text{unmix}}$ is the change in volume per unit mole at temperature T during phase separation, and $\Delta\alpha = \alpha_{\text{mix}} - \alpha_{\text{unmix}}$ is the change in expansion coefficient. The spinodal temperature θ_s is similarly affected:

$$\left(\frac{\partial \theta_s}{\partial P}\right)_T = \frac{\Delta v(T)}{2R \theta_c / \theta_s} [1 - T \Delta\alpha] \quad (6)$$

The expansion coefficient in glasses is generally a small number and, in most cases, $T \Delta\alpha \ll 1$. Therefore, only the first term of Eqs. 5 and 6 needs to be considered. The equations show that if there is expansion during phase separation $\beta < \beta_0$, there will be a reduction in transition temperature from the applied pressure, or positive stress.

3.1.2 Coefficient of Thermal Expansion

In analyzing the change in coefficient of thermal expansion with various heat-treatments, care must be taken to consider the density of the material at the beginning of the test. The test generally begins at room temperature and, therefore, the initial state of the glass is a function of the preceding cooling treatment through its density. Since the physical property of interest is the change in volume per unit of matter rather than per unit volume, the coefficient of thermal expansion must be normalized by the density in order to compare materials with different thermal histories. In this context therefore, we seek the change in density $\Delta\rho$ with temperature:

$$\frac{\Delta\rho}{\Delta T} = \rho \frac{\Delta\alpha}{\Delta T} = 3\rho\alpha \quad (7)$$

The density of each sample was measured prior to the measurement of coefficient of thermal expansion, and the change in density with temperature is plotted in figure 9. The data demonstrates no apparent change with degree of phase separation, therefore the normalized thermal expansion coefficient is not significantly altered by phase separation.

Since one of the phases is nearly pure silica,¹³ with an expansion coefficient near $0.5 \times 10^{-6}/^{\circ}\text{C}$, it is expected that the expansion coefficient of the individual phases will differ measurably. The average value of the bulk sample remained constant during phase separation, indicating that the dependence of the coefficient of thermal expansion on composition is linear along the tie line. This, however, does not imply that there will be no stress development during cooling of the two-phase structure, since there are differences in the microscopic coefficients of expansion. In fact,¹⁴ stresses are expected and have been observed in phase-separated glasses. The effect that these stresses can have on strength may be considerable and presents an interesting possible research project.

3.1.3 Discussion

By comparison with the miscibility surface of the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system,¹⁵ the composition of interest in this paper appears to be close to the critical value (number 34 in Ref. 15).² Further, the volume fractions, as measured from electron micrographs,² are nearly equal, therefore, it may be assumed that $\theta \sim \theta_c$ in our samples. This greatly simplifies Eqs. (5) and (6) to:

$$\left(\frac{\partial\theta}{\partial P}\right)_T = \frac{\Delta v(T)}{2R} = \left(\frac{\partial\theta_s}{\partial P}\right)_T \quad (8)$$

where $\Delta v(T)$ is a function of temperature.

The volume change per unit mole during phase separation was obtained from the density measurements as follows:

$$\Delta V = V_0 \left[\frac{1}{\rho_0} - \frac{1}{\rho_f} \right] \quad (9)$$

where ρ_0 and ρ_f are the densities of the mixed and unmixed systems, respectively. A comparison of the refractive index and density data at 565°C and 620°C, shows that the polarizability of the glass is not affected by phase separation and is not appreciably temperature dependent. Therefore, index data was also used to calculate the volume change. The results are shown in figure 10 where both density and index measurements are combined. The data show that Δv is very small at the transition temperature but increases linearly with $(T - T_c)$ as the temperature is lowered. The change in transition temperature is found by combining the results of the density measurements with Eqs. (8) and (9). In this material, the change is a decrease in transition temperature with applied pressure due to the decrease in density, but the effect is small in magnitude: $(\partial T_c / \partial P)_T$ is $-7 \times 10^{-3} \text{ }^\circ\text{K/kbar}$ at 660°C and $-19 \times 10^{-2} \text{ }^\circ\text{K/kbar}$ at 526°C. Measurements of the density change during phase separation in a soda-silica glass by L. D. Pye et al¹⁶ have shown no measurable change, indicating a linear dependence of molar volume on composition. Phase separation in this sample¹⁷ would therefore be unaffected by the application of pressure. It appears¹⁷ that the density change in soda-lime-silica glasses will be large and negative, also corresponding to a decrease in phase transition temperature with applied pressure. However, it is also possible for the density to increase during a phase transition. This will cause an increase in transition temperature with applied pressure, leading to a number of interesting problems in glass product manufacturing. Density data reported by Vashal et al¹⁸ on $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$ glasses doped with TiO_2 indicates the possible occurrence of this effect. Calculations based on Eqs. (8) and (9) show that a 5% difference in density between the mixed and unmixed states will lead to a change in transition temperature of 10°C per kilobar of pressure.

3.2 Chemical Durability

The glass rods used in this test were large enough to prevent reliable chemical durability measurements for heat-treatment times less than 15 minutes. The large size, however, was desirable to reduce the relative amount of surface material when the samples were crushed to powder. An analysis of the microstructure developed in fibers of this glass for heat-treatments shorter than 15 minutes proved very difficult, even at 620°C, due to the very small size of the structure and a lack of sufficient chemical differentiation between the phases to insure a proper etch for replication. However, from the viscosity data, it appears that relatively little structure develops in this glass for such short heat-treatments.

For heat-treatments lasting more than 15 minutes, as can be seen from figure 8, the chemical durability of the glass decreased significantly with advancing phase separation at each temperature. However, there is little temperature dependence.

Since chemical attack, or amount of leached alkali will be a sensitive function of available surface area and surface composition, it is likely to depend strongly upon phase composition, volume fraction and phase interconnectivity. However, it would appear to remain relatively independent of microstructure size.

Figure 11 shows a series of micrographs reprinted from Refs. 1 and 2 for the 620°C isotherm. This is representative of other temperatures. The microstructure size changes considerably, but both the phase volume fractions and interconnectivity remain relatively independent of heat-treatment time and temperature. Since the volume fractions are nearly equal for both phases and the interconnectivity is high, there is no development of isolated pockets of one phase as proposed by Mazurin et al¹⁹ to account for their observed changes in chemical durability.

The data shows no simple dependence on microstructure size since the durability varies little with temperature while microstructure size varies exponentially (see Ref. 1). There are no appreciable changes in volume fraction or interconnectivity, therefore, only the change in chemical composition of the phases can be the cause of the large deterioration in chemical durability observed in this glass during phase separation. As the material separates into phases more and less durable than the mixed state, the resultant average durability will decrease. This conclusion indicates that the two phases achieve compositional equilibrium relatively slowly due to the high viscosity. Since the chemical makeup of the equilibrium immiscible compositions varies little with temperature (a steep miscibility gap, as found in this system), the change in chemical durability will also be relatively temperature independent as we found in our measurements. Unfortunately, the titration measurements which were used in this test cannot detect a change in composition of the extract, since the ratios of alkali to other components are not known. A solution of this problem is achievable with a detailed chemical analysis of the extract by such techniques as atomic absorption spectroscopy. We are presently acquiring such an instrument and will study the problem in the following year. Some further support to our assertion is found in the analysis of the acid etches used to develop structure for replication and subsequent observation with electron microscopy. As stated in Ref. 1, stronger acid solutions were needed for samples treated at the shorter times which indicates smaller composition differences.

4. Summary and Conclusions

An equation was derived to describe the change in phase-transition temperature due to pressure applied isothermally. The equation is in differential form and is useful in calculating the change in transition temperature. An integration is possible to express the pressure dependence of the transition temperature explicitly if the change in isothermal compressibility can be measured.

Measurements of the coefficient of thermal expansion on a soda borosilicate glass widely used in industry for chemical glassware demonstrated no change with phase separation and a new equation was proposed for comparing measurements of thermal expansion coefficients in materials with different heat-treatments. Changes in density and index of refraction were observed and were analyzed in terms of a molar volume expansion during phase separation. The volume expansion implies a decrease in transition temperature with applied pressure. The magnitude of the effect is small in this material, but it was calculated that a 5% change in density during phase separation would lead to a change in transition temperature of 10°C per kilobar of applied pressure.

The chemical durability of the same glass was observed to decrease significantly (100 fold) with heat-treatment time. There was little dependence, however, on heat-treatment temperature. This data coupled with an analysis of electron micrographs taken on samples with similar heat-treatments suggest that the decrease in chemical durability arises from changes in the chemical composition of the phases.

5. References

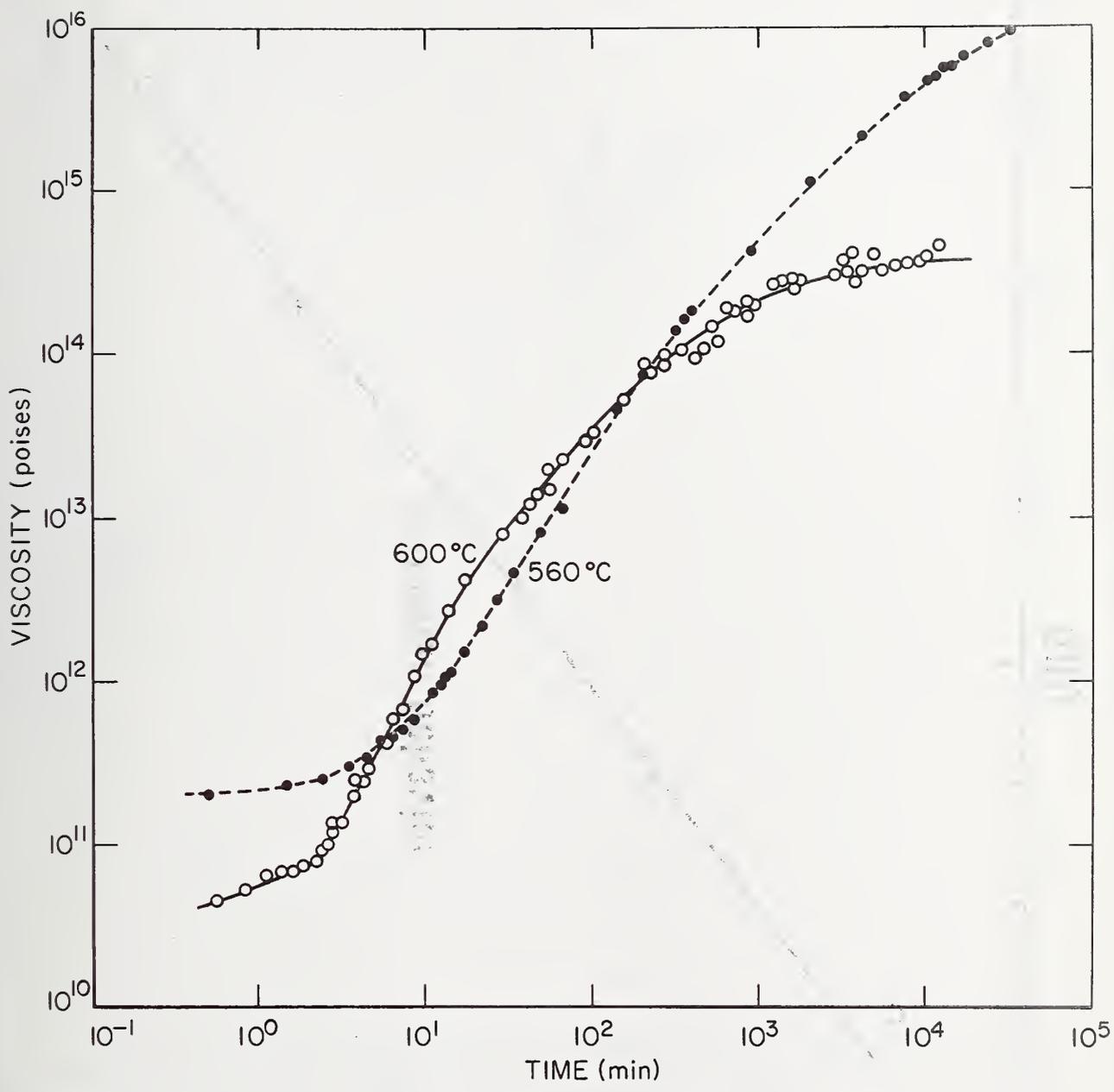
1. J. H. Simmons, S. A. Mills, A. Napolitano, D. H. Blackburn and W. Haller, NBS Tech. Note 792. (Sept. 1973).
2. J. H. Simmons, S. A. Mills and A. Napolitano, J. Am. Ceram. Soc. 57, 109 (1974).
3. R. Mahoney, G. R. Srinivasan, P. B. Macedo, A. Napolitano and J. H. Simmons, Phys. Chem. Glasses (Feb 1974), to be published.
4. J. H. Simmons, S. A. Mills and A. Napolitano, J. NonCrystalline Solids 14, 302 (1974).
5. S. Spinner and A. Napolitano, J. Res. NBS 70A, 147 (1966).
P. B. Macedo and A. Napolitano, J. Res. NBS 71A, 231 (1967).
6. "Test for the Density of Glass by the Sink-Float Comparator," Test C 729, Annual Book of ASTM Standards (American Soc. for Testing and Mat., Philadelphia, 1973).
7. A. Napolitano, J. H. Simmons, D. H. Blackburn and R. E. Chidester, J. Res. NBS (to be published).
8. "Resistance of Glass Containers to Chemical Attack," Test C 225, Annual Book of ASTM Standards (American Soc. for Testing and Mat., Philadelphia, 1973).
9. B. F. Howell, J. H. Simmons and W. Haller, "Chemical Durability Degradation of a Glass During Phase Separation" (in preparation).
10. J. B. Thompson, Jr., Researches in Geochemistry 2, 340 (1967).
11. W. Haller, D. H. Blackburn and J. H. Simmons, J. Amer. Ceram. Soc. 57, 120 (1974).
12. J. H. Simmons, "Theoretical Analysis of Miscibility Gaps in Ternary Systems" (in preparation).
13. E. A. Porai-Koohits, V. I. Averjanov, V. V. Golubkov and A. P. Titov, Mat. Res. Bull. 7, 1323 (1972).
14. F. Schill, Epitoanyag 24, 453 (1972).
15. W. Haller, D. H. Blackburn, F. E. Wagstaff and R. J. Charles, J. Amer. Ceram. Soc. 53, 34 (1970).
16. L. D. Pye, L. Ploetz and L. Manfredo, J. NonCrystalline Solids 14, 310 (1974).

17. I.S. Patel and S. M. Ohlberg, J. Appl. Phys. 43, 1636 (1972).
18. B. G. Varshal, N. M. Vaisfeld, G. B. Knyazher and L. M. Yusim, "Investigation of the Phase-Separation Processes in Titanium-Containing Glasses in the System SiO_2 - Al_2O_3 -CaO-MgO," Phase Separation Phenomena in Glasses, ed. E. A. Porai-Koshits (Structure of Glass, vol 8; Consultants Bureau, New York, 1973).
19. N. P. Danilova, O. V. Mazurin and T. S. Tsekhomskaja, IX International Congress on Glass 1, 825 (1971).

6. Figure Captions

- Figure 1 - Viscosity of soda borosilicate glass plotted as a function of heat-treatment time during phase separation at two temperatures. Note that due to the complexity of the effect, the viscosity at 600°C is higher than at 560°C for treatment times from 10 to 100 minutes.
- Figure 2 - Stress relaxation time plotted as a function of inverse temperature.
- Figure 3 - Dependence of refractive index on heat-treatment time for a variety of temperatures during phase separation.
- Figure 4 - Density and index data at 565°C.
- Figure 5 - Density and index data at 620°C.
- Figure 6 - Typical data from measurement of coefficient of thermal expansion.
- Figure 7 - Coefficient of thermal expansion of samples heat-treated at 585 and 620°C for the times shown.
- Figure 8 - Change in chemical durability for samples heat-treated at temperatures below the transition temperature, from 565 to 620°C for the times shown.
- Figure 9 - Plot of normalized coefficient of thermal expansion for samples heat-treated at 585 and 620°C for the times shown.
- Figure 10 - Change in molar volume during phase separation plotted as a function of temperature. The circles represent the density measurements and the crosses, the refractive index measurements.
- Figure 11 - Micrographs showing the structure developed during heat-treatments at 620°C for
- (a) 8 hours
 - (b) 48 hours
 - (c) 192 hours
 - (d) 768 hours

The bar is 1/2 μm .



STRESS RELAXATION TIME (min)

5

10

50

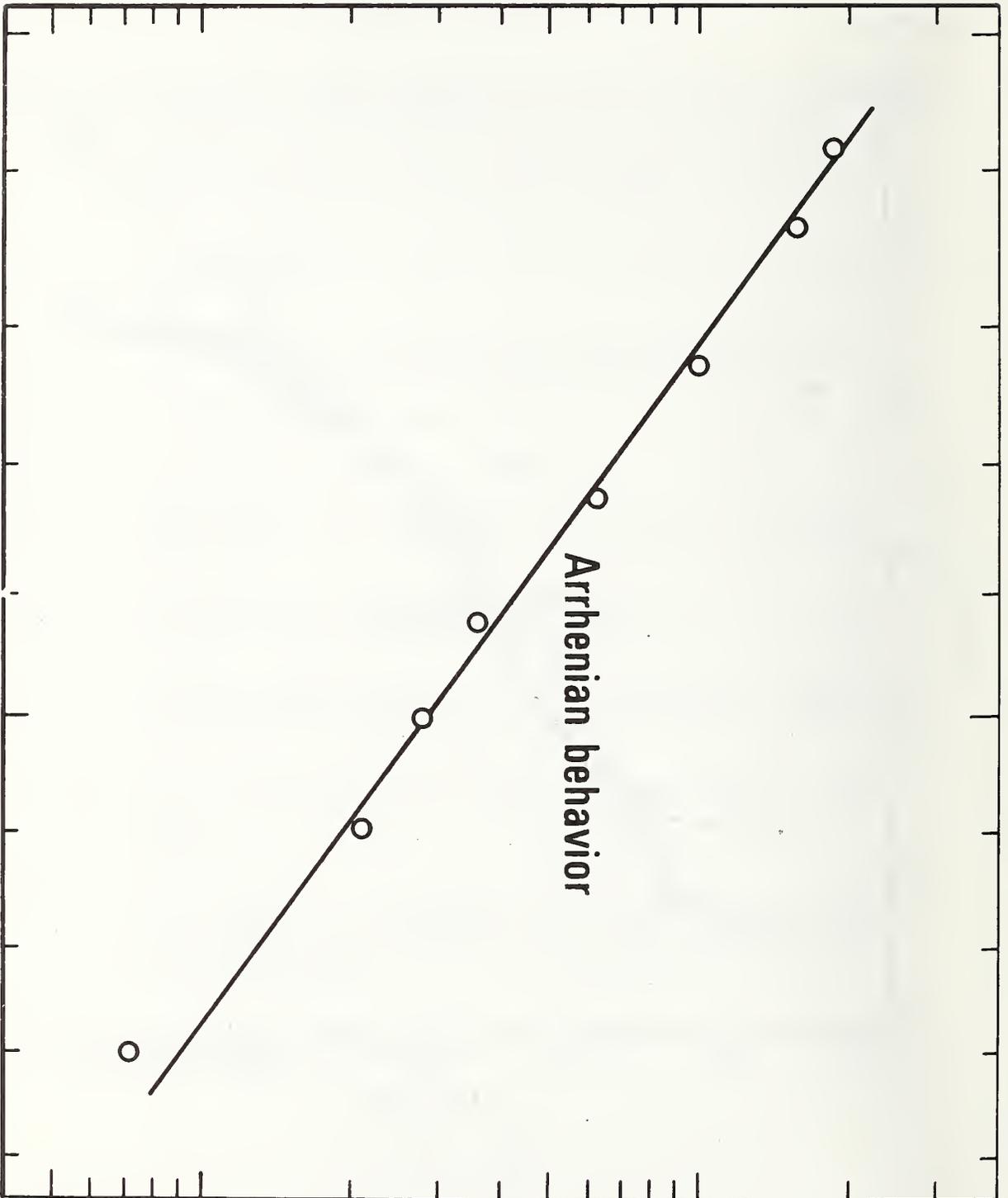
100

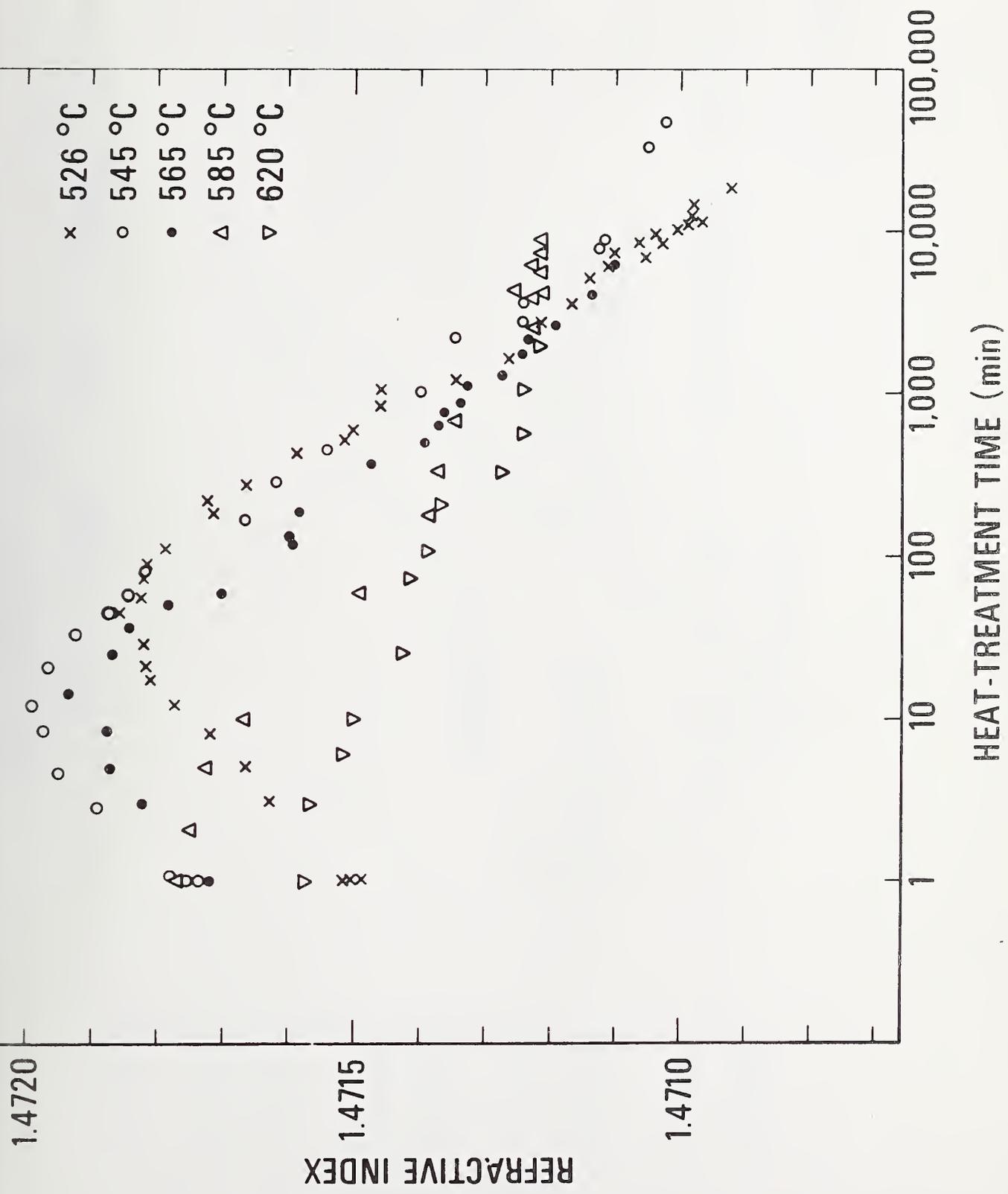
500

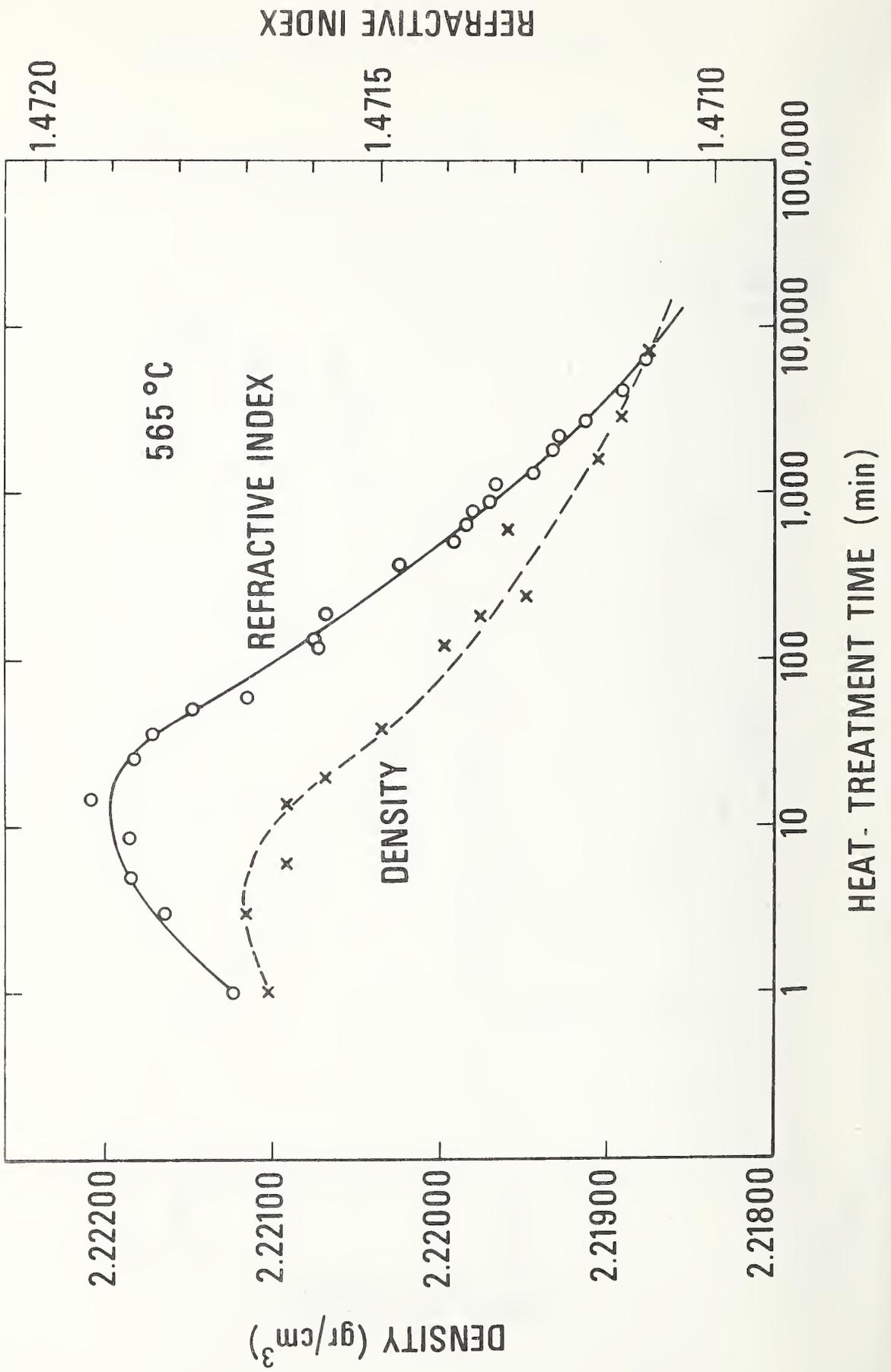
600

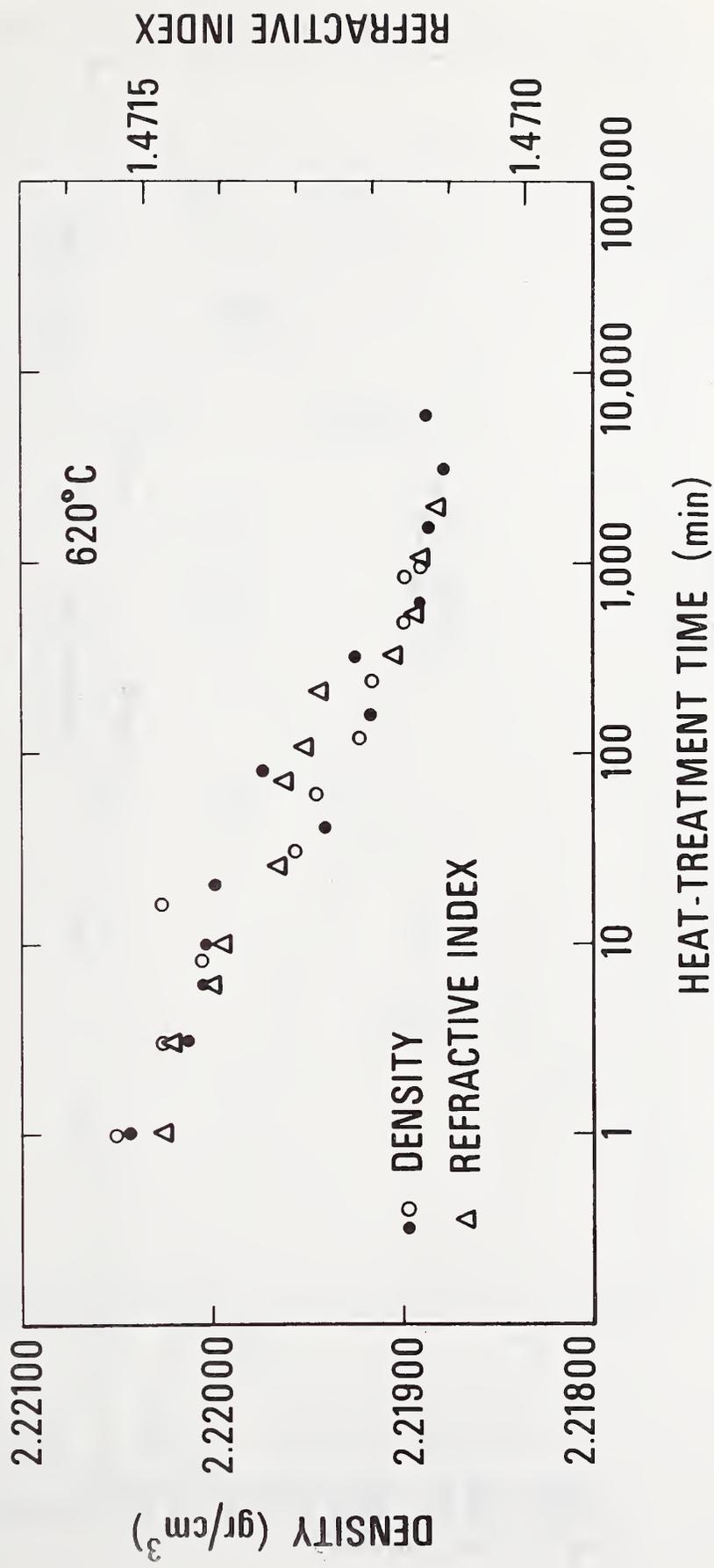
TEMPERATURE (°C)

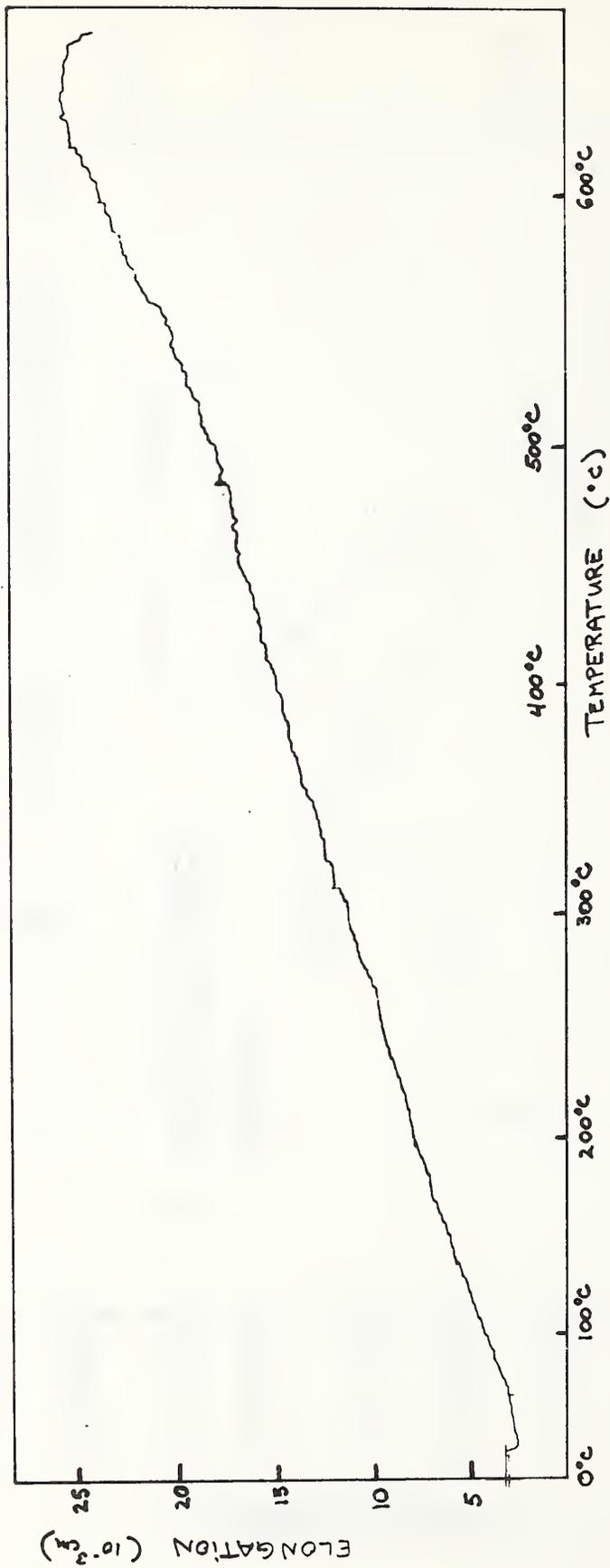
Arrhenian behavior

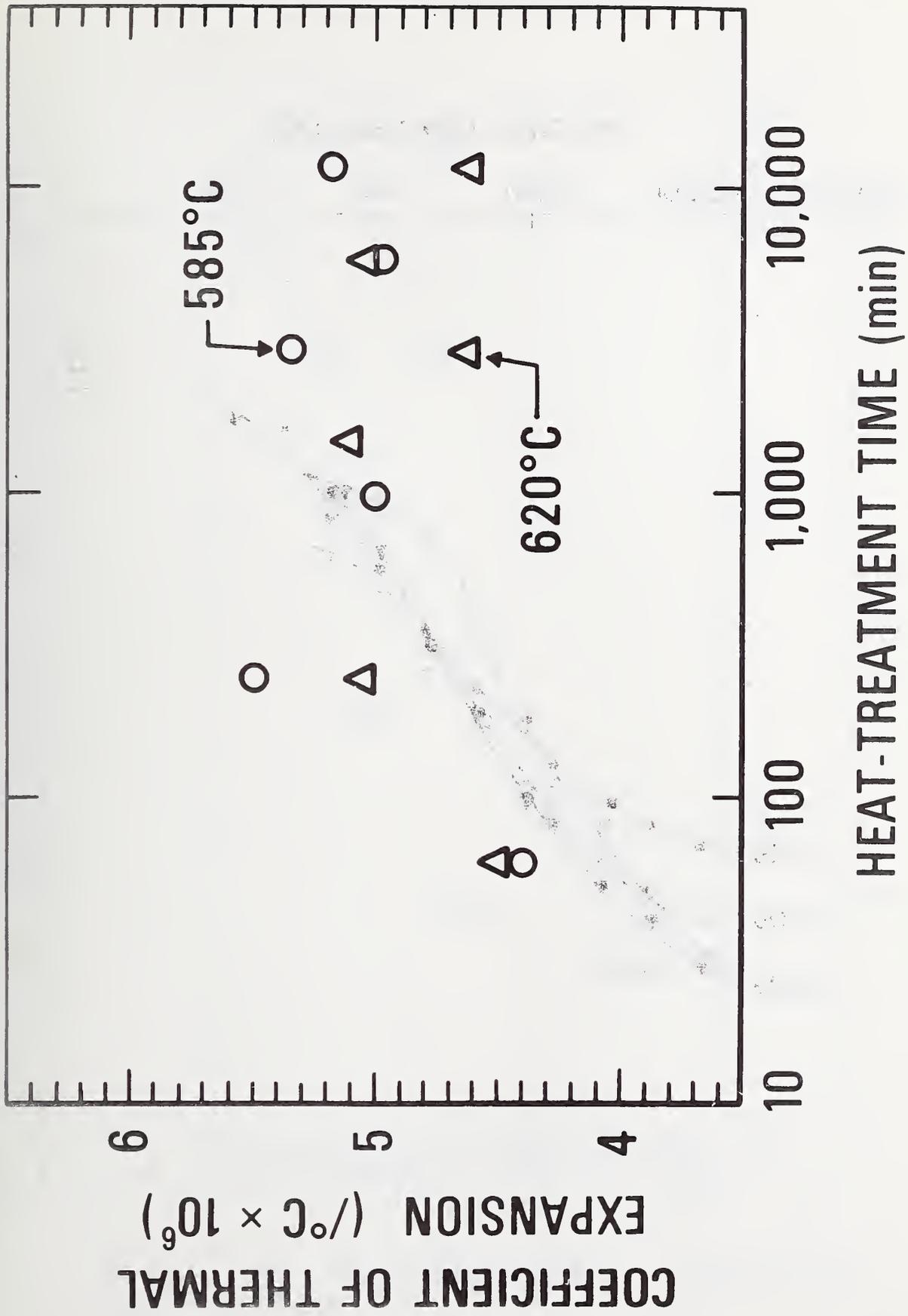


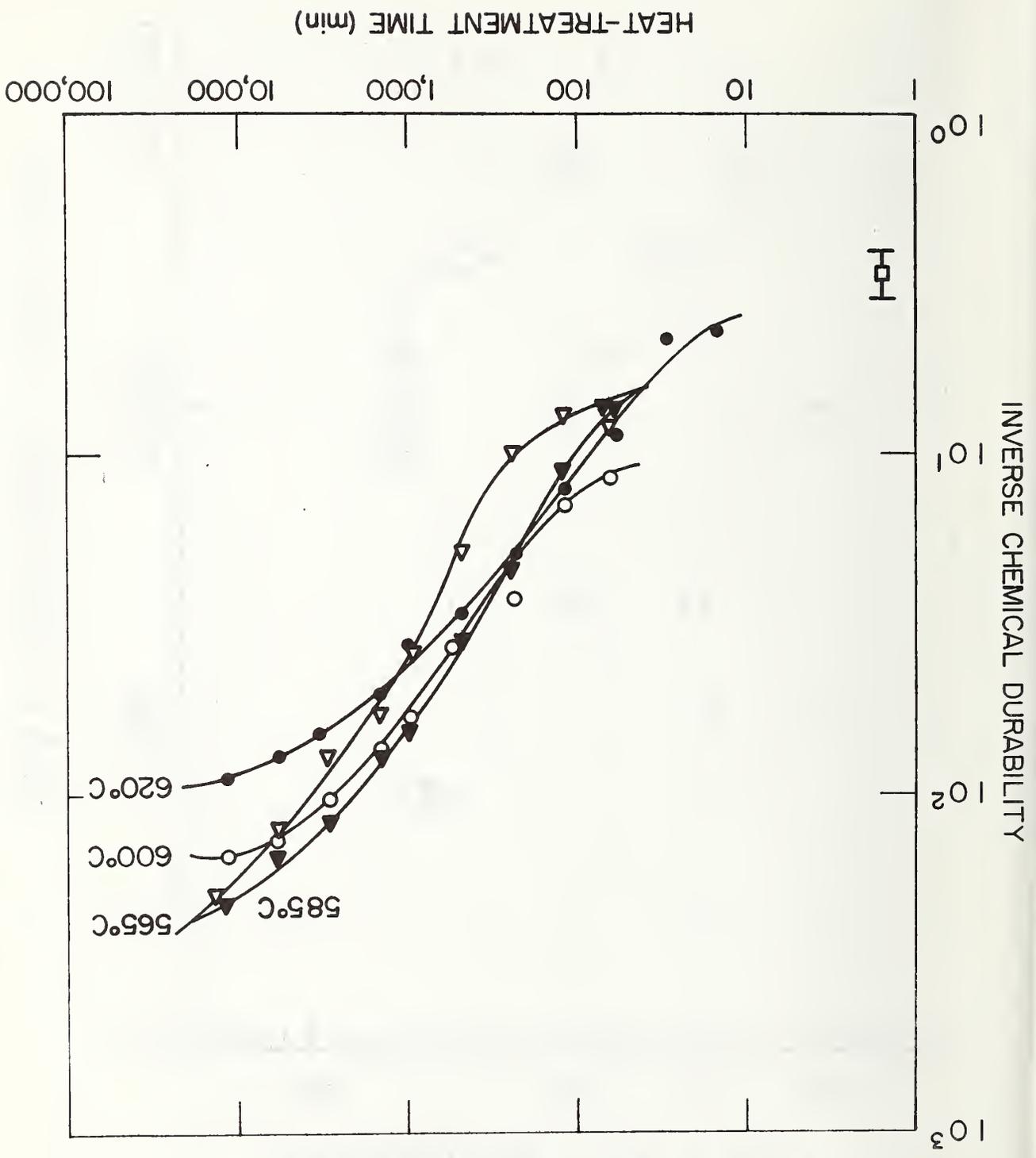


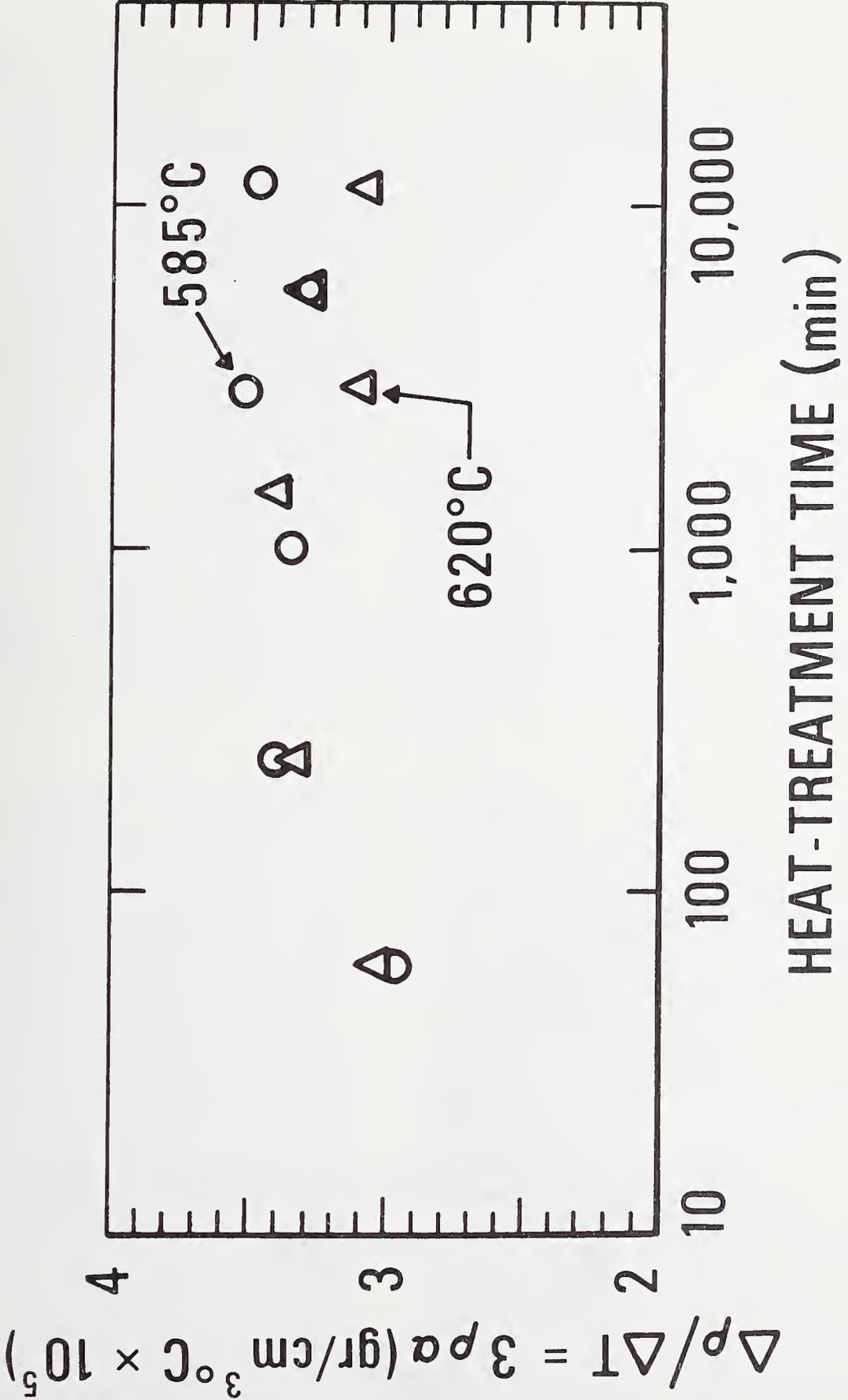


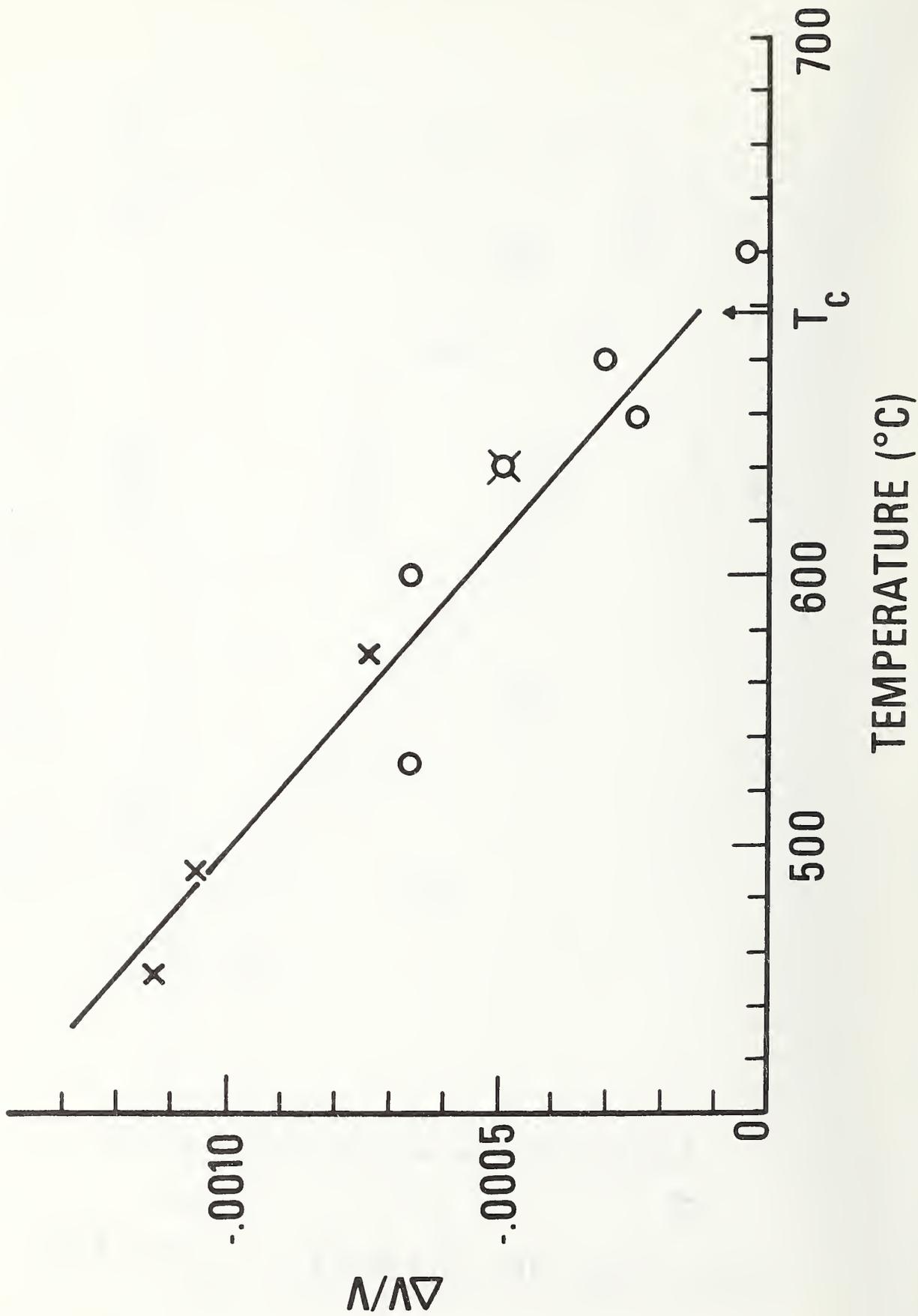


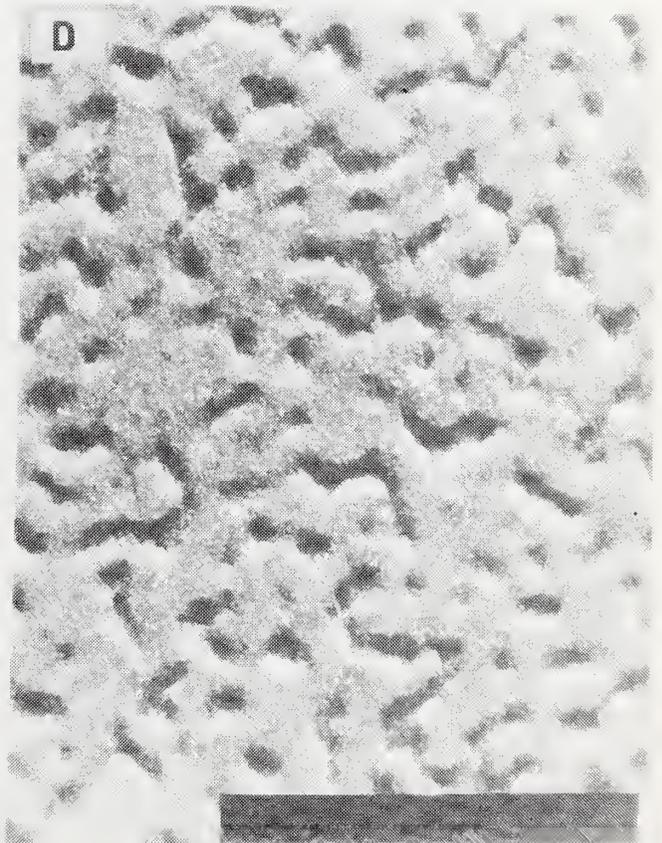
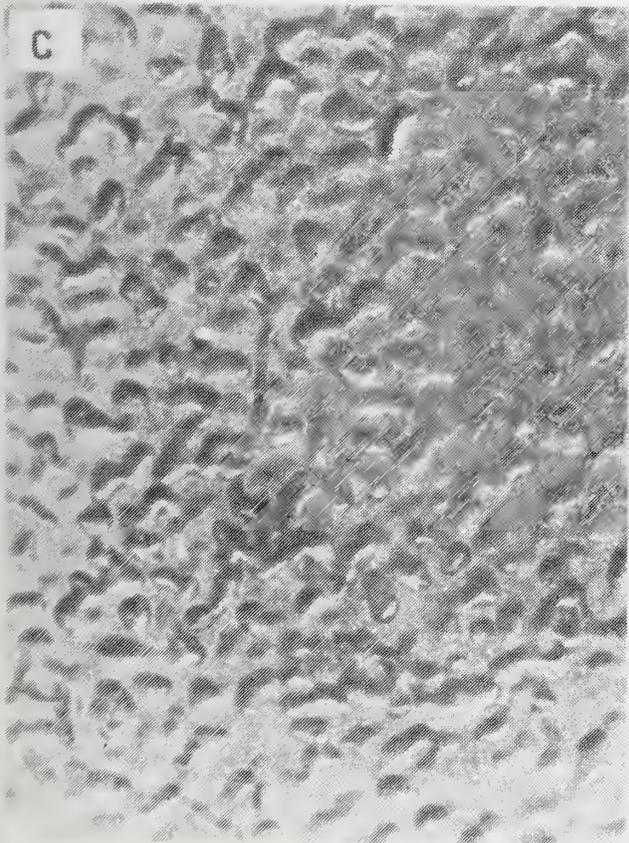
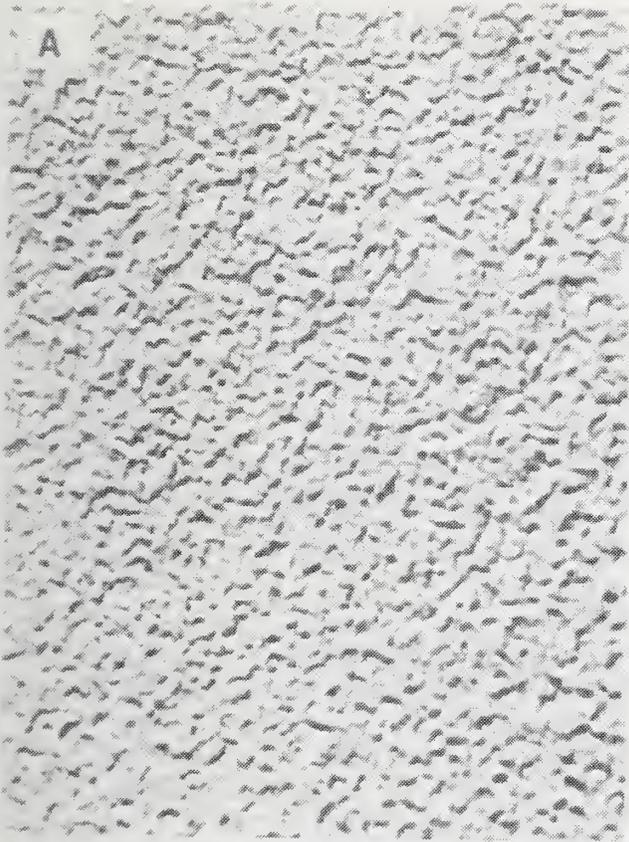












DISTRIBUTION LIST

Organization	Organization
Office of Naval Research Department of the Navy Attn: Code 471 Arlington, Virginia 22217	Director Naval Research Laboratory Attn: Technical Information Officer Code 2000 Washington, D. C. 20390
Director Office of Naval Research Branch Office 495 Summer Street Boston, Massachusetts 02210	Director Naval Research Laboratory Attn: Technical Information Officer Code 2020 Washington, D. C. 20390
Commanding Officer Office of Naval Research New York Area Office 207 West 24th Street New York, New York 10011	Director Naval Research Laboratory Attn: Technical Information Officer Code 6000 Washington, D. C. 20390
Director Office of Naval Research Branch Office 219 South Dearborn Street Chicago, Illinois 60604	Director Naval Research Laboratory Attn: Technical Information Officer Code 6100 Washington, D. C. 20390
Director Office of Naval Research Branch Office 1030 East Green Street Pasadena, California 91101	Director Naval Research Laboratory Attn: Technical Information Officer Code 6300 Washington, D. C. 20390
Commanding Officer Office of Naval Research San Francisco Area Office San Francisco, California 94102	Director Naval Research Laboratory Attn: Technical Information Officer Code 6400 Washington, D. C. 20390
Commanding Officer Naval Weapons Laboratory Attn: Research Division Dahlgren, Virginia 22448	Director Naval Research Laboratory Attn: Library Code 2029 (ONRL) Washington, D. C. 20390

Commander
Naval Air Systems Command
Department of the Navy
Attn: Code AIR 320A
Washington, D. C. 20360

Commander
Naval Air System Command
Department of the Navy
Attn: Code AIR 5203
Washington, D. C. 20360

Commander
Naval Ordnance Systems Command
Department of the Navy
Attn: Code ORD 033
Washington, D. C. 20360

Commanding Officer
Naval Air Development Center
Aeronautical Materials Div.
Johnsville
Attn: Code MAM
Warminster, Pa. 18974

Commanding Officer
Naval Ordnance Laboratory
Attn: Code 210
White Oak
Silver Spring, Maryland 20910

Commander
Naval Ship Systems Command
Department of the Navy
Attn: Code 0342
Washington, D. C. 20360

Commanding Officer
Naval Civil Engineering Laboratory
Attn: Code L70
Port Hueneme, California 93041

Commander
Naval Ship Engineering Center
Department of the Navy
Attn: Code 6101
Washington, D. C. 20360

Naval Ships R&D Laboratory
Annapolis Division
Attn: Code A800
Annapolis, Maryland 21402

Commanding Officer
Naval Ships R&D Center
Attn: Code 747
Washington, D. C. 20007

U. S. Naval Postgraduate School
Attn: Department of Chemistry
and Material Science
Monterey, California 93940

Commander Naval Weapons Center
Naval Weapons Center
Attn: Code 5560
China Lake, California 93555

Commander
Naval Underseas Warfare Center
Pasadena, California 92152

Scientific Advisor
Commandant of the Marine Corps
Attn: Code AX
Washington, D. C. 20380

Commanding Officer
Army Research Office, Durham
Box CM, Duke Station
Attn: Metallurgy & Ceramics Div.
Durham, North Carolina 27706

Office of Scientific Research
Department of the Air Force
Attn: Solid State Div. (SRPS)
Washington, D. C. 20333

Defense Documentation Center
Cameron Station
Alexandria, Virginia 22314

National Bureau of Standards
Attn: Metallurgy Division
Washington, D. C. 20234

National Bureau of Standards
Attn: Inorganic Materials Div.
Washington, D. C. 20234

Atomic Energy Commission
Attn: Metals & Materials Branch
Washington, D. C. 20545

Argonne National Laboratory
Metallurgy Division
P. O. Box 299
Lemont, Illinois 60439

Brookhaven National Laboratory
Technical Information Division
Attn: Research Library
Upton, Long Island, New York 11973

Library
Bldg. 50, Room 134
Lawrence Radiation Laboratory
Berkeley, California 94720

Los Alamos Scientific Laboratory
P. O. Box 1663
Attn: Report Librarian
Los Alamos, New Mexico 87544

Commanding Officer
Army Materials and Mechanics
Research Center
Attn: Res. Programs Office (AMXMR-P)
Watertown, Massachusetts 02172

Director
Metals & Ceramics Division
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

Commanding Officer
Naval Underwater Systems Center
Newport, Rhode Island 02844

Aerospace Research Laboratories
Wright-Patterson AFB
Building 450
Dayton, Ohio 45433

Defense Metals Information Center
Battelle Memorial Institute
505 King Avenue
Columbus, Ohio 43201

Army Electronics Command
Evans Signal Laboratory
Solid State Devices Branch
c/o Senior Navy Liaison Officer
Fort Monmouth, New Jersey 07703

Commanding General
Department of the Army
Frankford Arsenal
Attn: ORDBA-1320, 64-4
Philadelphia, Pennsylvania 19137

Executive Director
Materials Advisory Board
National Academy of Sciences
2101 Constitution Avenue, N. W.
Washington, D. C. 20418

NASA Headquarters
Attn: Code RRM
Washington, D. C. 20546

Air Force Materials Lab
Wright-Patterson AFB
Attn: MAMC
Dayton, Ohio 45433

Air Force Materials Lab
Wright-Patterson AFB
Attn: MAAM
Dayton, Ohio 45433

Deep Submergence Systems Project
Attn: DSSP-00111
Washington, D. C. 20360

Advanced Research Projects Agency
Attn: Director, Materials Science
Washington, D. C. 20301

Army Research Office
Attn: Dr. T. E. Sullivan
3045 Columbia Pike
Arlington, Virginia 22204

Department of the Interior
Bureau of Mines
Attn: Science & Engineering Advisor
Washington, D. C. 20240

Defense Ceramics Information Center
Battelle Memorial Institute
505 King Avenue
Columbus, Ohio 43201

National Aeronautics & Space Adm.
Lewis Research Center
Attn: Librarian
21000 Brookpark Rd.
Cleveland, Ohio 44135

Naval Missile Center
Materials Consultant
Code 3312-1
Point Mugu, California 93041

Commanding Officer
Naval Weapons Center Corona Labs.
Corona, California 91720

Commander
Naval Air Test Center
Weapons Systems Test Div. (Code 01A)
Patuxent River, Maryland 20670

Director
Ordnance Research Laboratory
P. O. Box 30
State College, Pennsylvania 16801

Director
Applied Physics Laboratory
Johns Hopkins University
8621 Georgia Avenue
Silver Spring, Maryland 20901

Director
Applied Physics Laboratory
1013 Northeast Fortieth St.
Seattle, Washington 98105

Materials Sciences Group
Code S130.1
271 Catalina Boulevard
Navy Electronics Laboratory
San Diego, California 92152

Dr. Waldo K. Lyon
Director, Arctic Submarine Laboratory
Code 90, Building 371
Naval Undersea R&D Center
San Diego, California 92132

Dr. R. Nathan Katz
Ceramics Division
U.S. Army Materials & Mechanics
Research Center
Watertown, Mass. 02172

SUPPLEMENTARY DISTRIBUTION LIST

Professor R. Roy
Materials Research Laboratory
Pennsylvania State University
University Park, Pennsylvania 16802

Professor D. H. Whitmore
Department of Metallurgy
Northwestern University
Evanston, Illinois 60201

Professor J. A. Pask
Department of Mineral Technology
University of California
Berkeley, California 94720

Professor D. Turnbull
Div. of Engineering and Applied Sci.
Harvard University
Pierce Hall
Cambridge, Massachusetts 02100

Dr. T. Vasilos
AVCO Corporation
Research and Advanced Development Div.
201 Lowell St.
Wilmington, Massachusetts 01887

Dr. H. A. Perry
Naval Ordnance Laboratory
Code 230
Silver Spring, Maryland 20910

Dr. Paul Smith
Crystals Branch, Code 6430
Naval Research Laboratory
Washington, D. C. 20390

Dr. A. R. C. Westwood
RIAS Division
Martin-Marietta Corporation
1450 South Rolling Road
Baltimore, Maryland 21227

Dr. W. Haller
Chief, Inorganic Glass Section
National Bureau of Standards
Washington, D. C. 20234

Dr. R. H. Doremus
General Electric Corporation
Metallurgy and Ceramics Lab.
Schenectady, New York 12301

Professor G. R. Miller
Department of Ceramic Engineering
University of Utah
Salt Lake City, Utah 84112

Dr. Philip L. Farnsworth
Materials Department
Battelle Northwest
P. O. Box 999
Richland, Washington 99352

Mr. G. H. Heartling
Ceramic Division
Sandia Corporation
Albuquerque, New Mexico 87101

Mr. I. Berman
Army Materials and Mechanics
Research Center
Watertown, Massachusetts 02171

Dr. F. F. Lange
Westinghouse Electric Corporation
Research Laboratories
Pittsburgh, Pennsylvania 15235

Professor H. A. McKinstry
Pennsylvania State University
Materials Research Laboratory
University Park, Pa. 16802

Professor T. A. Litovitz
Physics Department
Catholic University of America
Washington, D. C. 20017

Dr. R. J. Stokes
Honeywell Corporate Research Center
10701 Lyndale Avenue South
Bloomington, Minnesota 55420

Dr. Harold Liebowitz
Dean of Engineering
George Washington University
Washington, D. C. 20006

Dr. H. Kirchner
Ceramic Finishing Company
P. O. Box 498
State College, Pennsylvania 16801

Professor A. H. Heuer
Case Western Reserve University
University Circle
Cleveland, Ohio 44106

Dr. D. E. Niesz
Battelle Memorial Institute
505 King Avenue
Columbus, Ohio 43201

Dr. F. A. Kroger
University of Southern California
University Park
Los Angeles, California 90007

Dr. Sheldon M. Wiederhorn
National Bureau of Standards
Inorganic Materials Division
Washington, D. C. 20234

Dr. C. O. Hulse
United Aircraft Research Labs
United Aircraft Corporation
East Hartford, Connecticut 06108

Professor M. H. Manghnani
University of Hawaii
Hawaii Institute of Geophysics
2525 Correa Road
Honolulu, Hawaii 96822

Dr. Stephen Malkin
Department of Mechanical Engineering
University of Texas
Austin, Texas 78712

Prof. H. E. Wilhelm
Department of Mechanical Engineering
Colorado State University
Fort Collins, Colorado 80521

Stanford University
Dept. of Materials Sciences
Stanford, California 94305

Dr. R. K. MacCrone
Department of Materials Engineering
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. D. C. Mattis
Belfer Graduate School of Science
Yeshiva University
New York, New York 10033

Professor R. B. Williamson
College of Engineering
University of California
Berkeley, California 94720

Professor R. W. Gould
Department of Metallurgical
and Materials Engineering
College of Engineering
University of Florida
Gainesville, Florida 32601

Professor V. S. Stubican
Department of Materials Science
Ceramic Science Section
Pennsylvania State University
University Park, Pennsylvania 16802

Dr. R. C. Anderson
General Electric R&D Center
P. O. Box 8
Schenectady, New York 12301

Dr. Bert Zauderer
MHD Program, Advanced Studies
Room L-9513-VFSC
General Electric Company
P. O. Box 8555

Philadelphia, Pennsylvania 19101

Prof. C. F. Fisher, Jr.
Department of Mechanical and Aero-
space Engineering
University of Tennessee
Knoxville, Tennessee 37916

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBSIR 74-510	2. Gov't Accession No.	3. Recipient's Accession No.
4. TITLE AND SUBTITLE EFFECT OF PHASE SEPARATION ON THE PHYSICAL AND CHEMICAL PROPERTIES OF GLASSES-DENSITY AND CHEMICAL DURABILITY		5. Publication Date July 16, 1974	6. Performing Organization Code 313.02
7. AUTHOR(S) Joseph H. Simmons, Susan A. Mills and Barbara F. Howell	8. Performing Organ. Report No. NBSIR 74-510		
9. PERFORMING ORGANIZATION NAME AND ADDRESS NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234		10. Project/Task/Work Unit No. 3130426	11. Contract/Grant No. Naonr 12-73 NR 032-536
12. Sponsoring Organization Name and Complete Address (Street, City, State, ZIP) Office of Naval Research Department of the Navy Code 471 Washington, D.C. 20360		13. Type of Report & Period Covered Final Technical Report	14. Sponsoring Agency Code
15. SUPPLEMENTARY NOTES			
<p>16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)</p> <p>This report covers results from density and chemical durability measurements on a borosilicate glass widely used commercially for chemical glassware while the glass undergoes liquid-liquid immiscibility. A net decrease in density is observed during an isothermal heat-treatment below the transition temperature. This density or molar volume change is related to the effect of pressure on the phase transition temperature by means of equations derived herein. The chemical durability of the material is measured following the ASTM titration technique and shows a large degradation of chemical resistance to attack by water as a result of sub-immiscibility structure development. The effect is analyzed in terms of the change in composition of the phases associated with the immiscibility transition.</p>			
<p>17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)</p> <p>Borosilicate glass; chemical durability; density; immiscibility.</p>			
<p>18. AVAILABILITY</p> <p><input checked="" type="checkbox"/> Unlimited</p> <p>For Official Distribution. Do Not Release to NTIS</p> <p><input type="checkbox"/> Order From Sup. of Doc., U.S. Government Printing Office Washington, D.C. 20402, SD Cat. No. CI3</p> <p><input type="checkbox"/> Order From National Technical Information Service (NTIS) Springfield, Virginia 22151</p>		<p>19. SECURITY CLASS (THIS REPORT)</p> <p>UNCLASSIFIED</p>	<p>21. NO. OF PAGES</p> <p>31</p>
<p>20. SECURITY CLASS (THIS PAGE)</p> <p>UNCLASSIFIED</p>		<p>22. Price</p>	